OFFICE OF NAVAL RESEARCH

Grant N00014-90-J-1193

TECHNICAL REPORT No. 25

Scale-Invariant Theory of Optical Properties of Fractal Clusters

by

Vadim A. Markel, Leonid S. Muratov, Mark I. Stockman and Thomas F. George

Prepared for Publication

in

Scaling in Disordered Materials
Edited by J. P. Stokes
Materials Research Society, Pittsburgh

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

September 1990

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/90/TR-25	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260	7b. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Grant N00014-90-J-1193
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Scale-Invariant Theory of Optical Properties of Fractal Clusters

12. PERSONAL AUTHOR(S)

Vadim A. Markel, Leonid S. Muratov, Mark I. Stockman and Thomas F. George

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
	FROM _____ TO _____	September 1990	5

16. SUPPLEMENTARY NOTATION

Prepared for publication in Scaling in Disordered Materials, Edited by J. P. Stokes, Materials Research Society, Pittsburgh

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

FRACTAL CLUSTERS
OPTICAL PROPERTIES
SCALE-INVARIANT THEORY
EXTERNAL HAUSSDORF DIMENSION
DENSITY FLUCTUATIONS
LOCAL FIELDS

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Optical properties of fractal clusters are considered by means of a scale-invariant theory. Numerical simulations are carried out for three fractal types: self-avoiding walks, random walks and Witten-Sander's.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson	22b. TELEPHONE (Include Area Code) (202) 696-4410 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

Scaling in Disordered Materials, Proceedings of Symposium W (Extended Abstracts) Materials Research Society 1990 Fall Meeting, edited by J. P. Stokes

SCALE-INVARIANT THEORY OF OPTICAL PROPERTIES OF FRACTAL CLUSTERS

VADIM A. MARKEL[*], *LEONID S. MURATOV*[†], *MARK I. STOCKMAN*[*] and *THOMAS F. GEORGE*[‡]

[*] Institute of Automation & Electrometry, Siberian Branch of the USSR Academy of Sciences

[‡] Departments of Physics & Astronomy and Chemistry, Center for Electronic & Electro-optic Materials, 239 Fronczak Hall, State University of New York at Buffalo, Buffalo, NY 14260

INTRODUCTION

Fractals are scale self-similar mathematical objects possessing nontrivial geometrical properties [1,2]. There exist various physical realizations of fractals [3-5], and here we shall consider optical properties of what we believe to be one of the most important such realizations, namely, fractal clusters (to be named below simply as fractals).

A fractal cluster is a system of interacting material particles called monomers. This system is self-similar (in a statistical sense) with respect to scale transformations in an intermediate region of sizes r, $R_0 \ll r \ll R_c$, where R_0 is a characteristic separation between nearest monomers, and R_c is the cluster total size.

A consequence of the self-similarity is the scaling (power-like) form of the pair (density-density) correlation function $g(r)$, mean number N of the monomers in the the fractal and its mean density $\bar{\rho}$,

$$g(r) = (D/4\pi R_0^3)\,(r/R_0)^{D-3}, \quad N \sim (r/R_0)^D, \quad \bar{\rho} \sim (R_c/R_0)^{D-3}. \tag{1}$$

where the index D is the fractal (external Haussdorff) dimension. A fractal is called nontrivial if $D < 3$. As one can see from Eq. (1), the mean density of a nontrivial fractal is asymptotically (for $R_c \gg R_0$) zero. This feature, together with strong pair correlation, is the reason for the great role that the density fluctuations play in the fractals. Below we shall show that large correlated fluctuations of local fields play a decisive role in determining optical properties of fractals. In particular, there exists scaling of the optical absorption and the density of the dipole excitations (eigenstates) of the fractal.

The linear optical (dipole) polarizabilities of fractals have been studied theoretically [6-9]. However, the scale-invariant theory, which is the subject of the present report, has not been published in the literature.

FRACTAL OPTICAL PROPERTIES AND SCALING

Let us consider a model of a cluster as a system consisting of N polarizable particle (called monomers) located at the points $\mathbf{r}_i$, $i = 1 \ldots N$, with the dipole interaction between them, and $R_c \ll \lambda$, where λ is the light wavelength. The light-induced dipole (transition) moments $\mathbf{d}_i$ on monomers obey the well-known system of equations

$$d_{i\alpha} = \chi_0 E_\alpha^{(0)} - \chi_0 \sum_{j=1}^{N}{}' \left[\delta_{\alpha\beta} - 3n_\alpha^{(ij)} n_\beta^{(ij)}\right] r_{ij}^{-3} d_{j\beta}, \tag{2}$$

where the Greek subscripts stand for tensor components (summation over repeated indices is implied), and the Latin indices stand for ordinal numbers of monomers; χ_0 is the

dipolar polarizability of an individual (isolated) monomer: $\mathbf{E}^{(0)}$ is the electric field of the external (exciting) radiation: $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$; and $\mathbf{n}^{(ij)} = \mathbf{r}_{ij}/r_{ij}$.

The fractal specificity of the considered problem is due to the divergence at small r in the mean-field analog of Eq.(2), $\mathbf{E}^{(0)} - \chi_0 \int \mathrm{d} - 3\mathbf{r}(\mathbf{rd})/r^2 r^{-3} g(r)\mathrm{d}\mathbf{r}$ (cf. Refs. [8,9]). This divergence is an indication of the dominating role of large fluctuations and existence of scaling in fractals. In this brief report we can only outline the theory and then briefly discuss the results obtained.

The main object of the theory is the optical (dipole) polarizability $\chi(X)$ of the fractal (per one monomer) as a function of the variable $X = \mathrm{Re}\chi_0^{-1}$. The polarizability is formally found as a decomposition in terms of the exact eigenvectors and eigenvalues of Eq. (2). Using this decomposition, the exact sum rules for the polarizability are obtained as

$$\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{Im}\chi_{\alpha\beta}^{(i)}(X)\mathrm{d}X = \delta_{\alpha\beta} \ , \quad \mathbf{P}\int_{-\infty}^{\infty} \mathrm{Re}\chi_{\alpha\beta}^{(i)}(X)\mathrm{d}X = 0 \ , \quad \mathbf{P}\int_{-\infty}^{\infty} X\mathrm{Im}\chi(X)\mathrm{d}X = 0 \ . \tag{3}$$

where $\mathbf{P}$ denotes the principal value of integral.

The next step is to assume the scaling of dipole excitations of the fractal. Then the function $\mathrm{Im}\chi(X)$ can be shown to have the scaling form (note that $\mathrm{Re}\chi$ does not scale), if the resonance in the monomer has a high Q-factor, $Q = R_0^3 \mathrm{Im}\chi_0^{-1} \gg 1$. From (3) it follows that $\mathrm{Im}\chi$ scales as the function of $|X|$, thus having the form

$$\mathrm{Im}\chi(X) \sim R_0^3 \left(R_0^3|X|\right)^{d_o - 1} \ , \tag{4}$$

where the index d_0 is called the optical spectral dimension, $0 \le d_o \le 1$. Then, using the fact that $\mathrm{Im}\chi$ describes absorption and the total absorption of a fractal in the scaling region should not depend on choice of the minimum length R_0, from Eq. (4) we obtain the scaling transformation law $|X| \propto R_0^{-(3d_o - D)/(d_o - 1)}$. Using this, one can make sure that it possible to construct only one quantity L_X which has dimensionality of length and is invariant under the scaling transformation,

$$L_X \sim R_0 (R_0^3|X|)^{(d_o - 1)/(3 - D)} \ . \tag{5}$$

This quantity, in accord with Alexander's strong localization hypothesis [10], should coincide with the coherence length of the fractal excitations. Equation (5) defines, thus, the dispersion law for the dipole excitations of the fractal, with $1/L_X$ playing the role of wavevector. The conditions of scaling $R_0 \ll L_X \ll R_c$ and $X \gg R_0^{-3} Q^{-1}$ with the aid of Eqs. (5) and (1) are rewritten as

$$R_0^{-3} Q^{-1}, \ R_0^{-3} N^{(3/D - 1)/(1 - d_o)} \ll X \ll R_0^{-3} \ . \tag{6}$$

Hence, if the necessary condition $Q \gg 1$ is met, scaling occurs at small $|X|$. In the vicinity of the frequency ω_0 of the resonance in the monomer, the variable X is proportional to detuning $\Omega = \omega - \omega_0$, where ω is the light frequency. Hence, the scaling region does exist, occupying the center of the fractal absorption band. Equation (6) can be considered as a self-consistent validation of the scaling assumption.

Using the above mentioned exact decomposition of χ and Eqs. (3), one can show for the scaling region (6) that the following relation exists between $\mathrm{Im}\chi$ and the density $\nu(X)$ of the dipole excitations (eigenstates) of the fractal:

$$\mathrm{Im}\chi(X) = \frac{\pi}{3}\nu(X) \propto |X|^{d_o - 1} \ . \tag{7}$$

Thus, the density of states and optical absorption scale with the same exponent $d_o - 1$, and the index d_0 is the counterpart for the dipole excitations of the vibration (fracton) spectral dimensionality $\bar{\bar{d}}$ introduced by Alexander and Orbach [11]. The dipole excitations tend to surface plasmons in the trivial ($D - 3$) limit, while vibrations tend to phonons. The surface plasmons possess a spectral gap, while phonons do not, which is the reason why the dispersion law (5) differs from its counterpart [10,11]. For the same reason, the index d_o does not numerically coincide with $\bar{\bar{d}}$ (cf. $0 \le d_o \le 1$, while $0 \le \bar{\bar{d}} \le 3$).

The failure of the mean-field approach and existence of scaling imply that fluctuations of the local fields in the fractals play a decisive role in determining their optical properties. From the above mentioned expansion of χ in the terms of the fractal eigenstates, it is possible to obtain the exact relation (an analog of the optical theorem) describing the relative dispersion G of the local field $\mathbf{E}_i$ acting upon the i^{th} monomer in the fractal.

$$G \equiv \left\langle |\mathbf{E}_i|^2 \right\rangle / |\mathbf{E}^{(0)}|^2 = Q^{-1} (1 - Q^2 X^2) \, \mathrm{Im}\chi_{zz} \quad . \tag{8}$$

In the scaling region (6), from Eq. (8) it follows that

$$G \sim Q \, R_0^3 X^{d_0 - 1} \quad . \tag{9}$$

Thus, the fluctuations are large: the dispersion of $\mathbf{E}_i$ is proportional to $Q \gg 1$, reaching its maximum at the wings of the scaling region, i.e., for $|X| \lesssim 1$.

NUMERICAL SIMULATION.

Three types of fractals have been generated by the Monte-Carlo method: random walks ($D = 2$), self-avoiding random walks ($D \approx 1.7$) and the Witten-Sander clusters [12] ($D \approx 2.5$). The mean number of monomers in the cluster was $N = 25 - 50$, and the number of clusters was from several hundred to thousand. For each cluster the fundamental system (2) was solved, and averaging over different fractals was performed. The numerical results show that the absorption and density of states obey the scaling prediction (4) and (7). The example of such results is presented in Fig. 1. The the values found for the d_o-exponent from the figure and similar data for other fractals are given in Table 1.

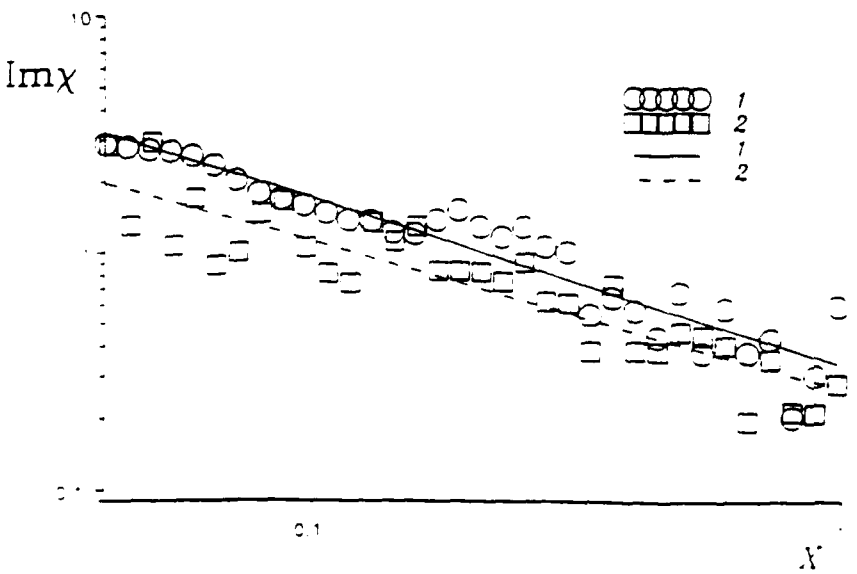

Fig. 1
Double-logarithmic plot of $\mathrm{Im}\chi(X)$ calculated directly (circles) and expressed through the eigenstate density with the aid of Eq. (7) (squares). The straight lines are found by the linear regression.

Table 1

Fractal type:	Self-avoiding walks	Random walks	Witten-Sander's
d_o found from Imχ:	0.43 ± 0.03	0.38 ± 0.03	0.49 ± 0.02
d_o from eigenstate density:	0.54 ± 0.08	0.33 ± 0.05	0.51 ± 0.06

CONCLUDING DISCUSSION

The scaling of optical absorption in nontrivial fractals is suggested by the failure of the mean-field approach. Assuming scaling (4), we have finally found the condition (6) of it, which means that the scaling assumption is self-consistent. Scaling is confirmed by numerical simulation, and the values of d_o are found for three types of fractals. Also, scaling is intimately coupled to large fluctuation of local fields in nontrivial fractals. Such fluctuations, as shown in the framework of the binary approximation [13], bring about giant enhancement of the nonlinear parametric scattering of light from fractals. The selective photomodification of fractals is also due to these fluctuations [14]. The features mentioned indicate the fractals to be promising media for nonlinear optics and optical information processing.

ACKNOWLEDGMENTS

This research was supported by the office of Naval Research and the National Science Foundation under Grant CHE-8922288.

REFERENCES

1. B. M. Mandelbrot, *Fractals, Form, Chance, and Dimension* (Freeman, San Francisco, 1977).
2. B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).
3. Ya. B. Zel'dovich and D. D. Sokolov, Uspekhi fiz. nauk **146**, 493 (1985) [Translation: Sov. Phys. Usp. **28**, 608 (1985)].
4. L. Pietroniero and E. Tosatti, Eds., *Fractals in Physics* (North-Holland, Amsterdam, 1986).
5. B. M. Smirnov, Uspekhi fiz. nauk **149**, 177 (1986) [Translation: Sov. Phys. Usp. **29**, 481 (1986)].
6. M. V. Berry and I. C. Percival, Opt. Acta **33**, 577 (1986).
7. P. M. Hui and D. Stroud, Phys. Rev. B **33**, 2163 (1986).
8. V. M. Shalaev and M. I. Stockman, ZhETF **92**, 509 (1987) [Translation: Sov. Phys. JETP **65**, 287 (1987)].
9. V. M. Shalaev and M. I. Stockman, Z. Phys. D **10**, 71 (1988).
10. S. Alexander, Phys. Rev. B **40**, 7953 (1989).
11. S. Alexander and R. Orbach, J. Physique Lett. **43**, 625 (1982).
12. T. A. Witten and L. M. Sander, Phys. Rev. B **27**, 5686 (1983).
13. A. V. Butenko, V. M. Shalaev and M. I. Stockman, ZhETF **94**, 107 (1988) [Translation: Sov. Phys. JETP **67**, 60 (1988)]; Z. Phys. D. **10**, 81 (1988).
14. T. T. Rantala, M. I. Stockman and T. F. George, in the present Proceedings.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

David Taylor Research Center (1)
Dr. Eugene C. Fischer
Annapolis, MD 21402-5067

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. David L. Nelson (1)
Chemistry Division
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Bernadette Eichinger (1)
Naval Ship Systems Engineering
Station
Code 053
Philadelphia Naval Base
Philadelphia, PA 19112

Dr. Sachio Yamamoto (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

FY90 Abstracts Distribution List for Solid State & Surface Chemistry

Professor John Baldeschwieler
Department of Chemistry
California Inst. of Technology
Pasadena, CA 91125

Professor Paul Barbara
Department of Chemistry
University of Minnesota
Minneapolis, MN 55455-0431

Dr. Duncan Brown
Advanced Technology Materials
520-B Danury Rd.
New Milford, CT 06776

Professor Stanley Bruckenstein
Department of Chemistry
State University of New York
Buffalo, NY 14214

Professor Carolyn Cassady
Department of Chemistry
Miami University
Oxford, OH 45056

Professor R.P.H. Chang
Dept. Matls. Sci. & Engineering
Northwestern University
Evanston, IL 60208

Professor Frank DiSalvo
Department of Chemistry
Cornell University
Ithaca, NY 14853

Dr. James Duncan
Federal Systems Division
Eastman Kodak Company
Rochester, NY 14650-2156

Professor Arthur Ellis
Department of Chemistry
University of Wisconsin
Madison, WI 53706

Professor Mustafa El-Sayed
Department of Chemistry
University of California
Los Angeles, CA 90024

Professor John Eyler
Department of Chemistry
University of Florida
Gainesville, FL 32611

Professor James Garvey
Department of Chemistry
State University of New York
Buffalo, NY 14214

Professor Steven George
Department of Chemistry
Stanford University
Stanford, CA 94305

Professor Tom George
Dept. of Chemistry & Physics
State University of New York
Buffalo, NY 14260

Dr. Robert Hamers
IBM T.J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

Professor Paul Hansma
Department of Physics
University of California
Santa Barbara, CA 93106

Professor Charles Harris
Department of Chemistry
University of California
Berkeley, CA 94720

Professor John Hemminger
Department of Chemistry
University of California
Irvine, CA 92717

Professor Roald Hoffmann
Department of Chemistry
Cornell University
Ithaca, NY 14853

Professor Leonard Interrante
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12181

Professor Eugene Irene
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. Sylvia Johnson
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. Zakya Kafafi
Code 6551
Naval Research Laboratory
Washington, DC 20375-5000

Professor Larry Kesmodel
Department of Physics
Indiana University
Bloomington, IN 47403

Professor Max Lagally
Dept. Metal. & Min. Engineering
University of Wisconsin
Madison, WI 53706

Dr. Stephen Lieberman
Code 522
Naval Ocean Systems Center
San Diego, CA 92152

Professor M.C. Lin
Department of Chemistry
Emory University
Atlanta, GA 30322

Professor Fred McLafferty
Department of Chemistry
Cornell University
Ithaca, NY 14853-1301

Professor Horia Metiu
Department of Chemistry
University of California
Santa Barbara, CA 93106

Professor Larry Miller
Department of Chemistry
University of Minnesota
Minneapolis, MN 55455-0431

Professor George Morrison
Department of Chemistry
Cornell University
Ithaca, NY 14853

Professor Daniel Neumark
Department of Chemistry
University of California
Berkeley, CA 94720

Professor David Ramaker
Department of Chemistry
George Washington University
Washington, DC 20052

Dr. Gary Rubloff
IBM T.J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

Professor Richard Smalley
Department of Chemistry
Rice University
P.O. Box 1892
Houston, TX 77251

Professor Gerald Stringfellow
Dept. of Matls. Sci. & Engineering
University of Utah
Salt Lake City, UT 84112

Professor Galen Stucky
Department of Chemistry
University of California
Santa Barbara, CA 93106

Professor H. Tachikawa
Department of Chemistry
Jackson State University
Jackson, MI 39217-0510

Professor William Unertl
Lab. for Surface Sci. & Technology
University of Maine
Orono, ME 04469

Dr. Terrell Vanderah
Code 3854
Naval Weapons Center
China Lake, CA 93555

Professor John Weaver
Dept. of Chem. & Mat. Sciences
University of Minnesota
Minneapolis, MN 55455

Professor Brad Weiner
Department of Chemistry
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Professor Robert Whetten
Department of Chemistry
University of California
Los Angeles, CA 90024

Professor R. Stanley Williams
Department of Chemistry
University of California
Los Angeles, CA 90024

Professor Nicholas Winograd
Department of Chemistry
Pennsylvania State University
University Park, PA 16802

Professor Aaron Wold
Department of Chemistry
Brown University
Providence, RI 02912

Professor Vicki Wysocki
Department of Chemistry
Virginia Commonwealth University
Richmond, VA 23284-2006

Professor John Yates
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260